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## A COMPARISON OF "TEMPORARY HARDNESS" WITH ALKALINITY IN NATURAL WATERS

BY A. M. BUSWELL

The purpose of this brief paper is to call attention to a careless or incorrect use of certain terms for the description of the mineral salts in solution in natural waters. It is in order therefore to recall a few well-known definitions before presenting the data and conclusions regarding these terms.

The total hardness of a water is a measure of the calcium and magnesium salts, carbonates, sulphates, etc., present in the water.

The temporary hardness is the amount of calcium and magnesium salts which are precipitated by thorough boiling. This precipitation is due in part to the decomposition of bicarbonates to form the less soluble carbonates, and in part to the hydrolysis of carbonates and sulphates.

The permanent hardness is the hardness after boiling.

The alkalinity is the sum of the carbonates and hydroxides of the alkali and alkaline-earth metals.

So many writers<sup>1</sup> state, or lead one to infer, that "temporary hardness" in water is equal, or nearly equal, to the "alkalinity" that it seems worth while to call attention to a few typical analyses in which the temporary hardness differs *widely* from the alkalinity. Data will therefore be presented to show that there is a very considerable alkalinity in many waters after boiling.

Mason<sup>2</sup> states that not quite all the bicarbonates are precipitated by boiling and cites an example of a water showing:

<sup>1</sup> Norton and Knowles, A Study of Indicators for the Determination of Temporary Hardness in Water. *J. Am. Chem. Soc.*, 38, 877.

Mason, Examination of Water, p. 26 et seq.

Woodman and Norton, Air, Water, and Food, p. 92.

Purvis and Hodgson, The Chemical Examination of Water, Sewage, and Food, p. 14.

Bailey, Sanitary and Applied Chemistry, p. 67.

<sup>2</sup> Mason, *Loc. cit.*, p. 27.

Before boiling alkalinity = 259 parts per million  $\text{Ca CO}_3$

After boiling alkalinity = 28 parts per million  $\text{Ca CO}_3$

Since  $\text{MgCO}_3$  is soluble to the extent of 100 parts per million,<sup>3</sup> and  $\text{CaCO}_3$  is soluble to the extent of 18 parts per million, and since  $\text{Na}_2\text{CO}_3$  is not uncommon in water from certain localities, it is obvious that many waters will show a much greater alkalinity after boiling than even the one cited by Mason. Accordingly tests were made on five samples of hard water having the following analyses:<sup>4</sup>

*Analyses of hard water*

Parts per million

	1	2	3	4	5
Alkalinity.....	208	222	341	265	880
Total hardness by soap method.....	245	360	630	380	630
Calcium hardness <sup>5</sup> .....	190	210	430	230	485
Magnesium hardness .....	55	150	200	150	145
Free carbon dioxide.....	11	7	30	7	61
Chlorides.....	94	16	235	33	800
Sulphates.....	3	266	188	208	21

These waters are harder than many natural waters, but they are typical of samples received in the laboratories of water-softening concerns, and may with perfect fairness be taken for comparison of "temporary hardness" with alkalinity. Sample 1 had been standing for some time before the boiling tests, mentioned below, were carried out. Its alkalinity had dropped from 208 to 90 and a considerable precipitate of calcium carbonate had formed on the sides and bottom of the container. Samples 2 and 5 contain considerable amounts of magnesium salts. Sample 5 also shows considerable excess of alkalinity over total hardness, indicating the presence of sodium and potassium carbonates.

The alkalinity of these samples was determined before and after boiling by titrating with  $\frac{N}{50}$  sulphuric acid in the presence of methyl-orange indicator. The results are given below.

<sup>3</sup> Kaye and Laby, Physical and Chemical Constants, p. 109 et seq.

<sup>4</sup> Samples were obtained through the courtesy of The Permutit Company,

<sup>5</sup> Winkler, Bestimmung des in natürlichen Wasser enthaltenen Calciums und Magnesiums. *Zeit. f. Anal. Chem.*, 40, 82.

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	(1)	(2)	(3)	(4)	(5)
Alkalinity before boiling.....	90	222	341	265	880
Alkalinity after boiling.....	63	110	90	170	345

From the above data it is evident that the term "temporary hardness" is not only not synonymous with, but in many cases does not even approximate the "alkalinity." All five samples showed considerable alkalinity after boiling. Furthermore, the term "temporary hardness" has no greater practical value than to estimate the scale which will form in a tea-kettle. It bears no definite relation to the scale formed in a boiler, for at elevated temperatures and pressures other salts than the bicarbonates are hydrolyzed and decomposed. Nor does the knowledge of the "temporary hardness" aid in calculating the lime required to soften a water by the lime-soda process. The term "temporary hardness" should be abandoned, and only the terms, "total hardness" and "alkalinity" should be used in describing the presence of calcium and magnesium salts in natural waters.